

PATENT SPECIFICATION

(11) 1 283 737

NO DRAWINGS

- (21) Application No. 40438/69 (22) Filed 13 Aug. 1969
(31) Convention Application No. 757488 (32) Filed 4 Sept. 1968 in
(33) United States of America (US)
(45) Complete Specification published 2 Aug. 1972
(51) International Classification B01J 11/08 11/22 C07C 69/14
(52) Index at acceptance
B1E 20Y 21Y 230 25Y 271 303 308 330 331 332 33Y 342 343
344 34Y 351 352 35Y 360 36Y 370 374 375 37Y 383
38Y 390 391 392 39Y 400 401 40Y 410 411 412 413
41Y 420 421 422 42Y 47Y 517 518 519 520 521 522
523 524 525 526 527 528 529 530 531 532 533 534
535 536 537 550 55Y 562 572 593 665 667 691
C2C 3A10E3A2 3A10E5J



(54) METHOD OF CATALYST PREPARATION

- (71) We, NATIONAL DISTILLERS & CHEMICAL CORPORATION, a corporation organized and existing under the laws of the State of Virginia, United States of America, located at 99 Park Avenue, New York City, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—
- This invention relates to a method for preparing a supported metal catalyst.
- Numerous catalyst preparation methods have been proposed heretofore for the deposition of metals on an inert carrier. Many of these processes involve unduly complicated and/or time consuming treatments which appreciably increase the cost of the catalyst. In addition, these methods have generally produced a final catalyst wherein the metal is confined entirely to the surface of the carrier or is distributed throughout the carrier. Neither of these results is desirable for certain commercial applications of the catalysts. If the metal is confined to the surface of the carrier, substantial physical losses of the catalytically active component tend to result from abrasion, etc. On the other hand, if the metal is distributed throughout the carrier, a substantial amount of the catalytic metal becomes unavailable for the reaction. Either the loss of catalyst or the inaccessibility of the catalyst are serious problems, especially where high priced metals such as palladium or platinum metals are employed. Obviously varying degrees of metal penetration into the inert carrier may provide particular advantages for certain uses in contrast to surface or thorough distribution. It would be desirable to have available a method for preparing a supported metal catalyst which would also provide the ability to readily control the degree to which the metal penetrates the inert carrier.
- The aforementioned disadvantages also apply when the deposition of two or more metals is attempted. In U.S. Patent No. 3,271,327, for example, a process is described wherein the inert carrier and the palladium salt are aged for extended periods at a pH required for the precipitation of the palladium metal as the oxide on the surface of the carrier. This procedure is obviously time consuming, does not permit control of the degree of penetration and cannot be employed where two metals of different isoelectric points are to be deposited together.
- The present invention provides a method of preparing a supported metal catalyst which comprises depositing at least one metal compound on a porous catalyst support by contacting the support with a solution of at least one compound of at least one metal selected from platinum, ruthenium, rhodium, palladium, iridium, osmium, rhenium, vanadium, titanium, tungsten, molybdenum, gold, silver, cobalt, nickel and the lanthanide metals, and converting the deposited compound or compounds to the metallic state, the porous catalyst support contacted with the said solution being one which has been impregnated with an alkaline solution and which is from 25 to 90%, preferably from 25 to 75% saturated with water or an alcohol.
- The said metal compound solution may additionally include at least one metal selected from chromium, manganese, iron, copper, cadmium, tin, lead, aluminium and mercury.
- The porous supports which may be employed in the method of this invention include alumina, silica, silica-alumina, silicic acid, carbon, or mixtures of barium, strontium or calcium carbonates with silica

and/or alumina. For many purposes the use of an alumina support is especially preferred. The inert support (carrier) is not necessarily limited to the foregoing materials, since a wide variety of porous supports can be effectively utilized. The carrier may be in the form of pellets, preferably having a particle size of at least $1/32$ inch, and most preferably within the range of $1/16$ to $3/8$ inch. The shape of the support pellets is preferably spherical, although a support in the form of chips or powder may also be employed.

Impregnation of the porous carrier with an alkaline solution may be effected by contact with an alkaline aqueous or alcoholic solution of, for example, sodium hydroxide, sodium carbonate, sodium bicarbonate, disodium hydrogen phosphate, potassium acetate, potassium hydroxide, ammonium phosphate, or mixtures thereof. Hydroxides and carbonates are preferred. The contacting can be accomplished by such conventional treatments as spraying, washing or immersion. If an alcoholic solution is used, the alcohol will generally be a lower alkanol having from 1 to 4 carbon atoms. Typical alcohols include methanol, ethanol, propanol, isopropanol, t-butanol, as well as mixtures thereof. The concentration of the alkaline material in the aqueous or alcoholic solution may for example vary from 0.5 to 20%, preferably from 1 to 10% by weight.

In accordance with one of the preferred procedures of this invention porous carrier pellets are immersed in an alkaline aqueous or alcoholic solution and are then drained free of excess solution. Another preferred embodiment involves spraying the porous carrier pellets with the alkaline solution.

In one embodiment, following the initial treatment of the carrier pellets with the alkaline solution, the pellets are partially dried to lower the water or alcohol content to a range of from 25 to 90%, preferably from 25 to 75%, of saturation. Conventional drying procedures may be employed here, although preferably a warm, inert gaseous stream is passed through or over the carrier pellets. The gases which may be used for this purpose include air, nitrogen, and argon, as well as mixtures thereof. The temperature of the gaseous stream is not critical and may for example vary from 40° to 150°C . The degree to which the water or alcohol content in the carrier is lowered is an important feature of the present invention, since it influences the degree of penetration of metal compound into the carrier during the subsequent step. For most purposes it has been found advantageous to limit the depth of penetration to up to 50% of the carrier pellet radius.

Obviously other variables such as the particular carrier, the total metal compounds

to be deposited, as well as the strength and concentration of the alkaline solution are factors which will influence penetration but they can be readily determined empirically.

The next procedural step involves contacting, e.g. spray coating, the carrier pellets with the metal compound solution. The metal salts which may be used include the halides, sulfates, nitrates, and acetates. When mixtures of metals are to be simultaneously deposited, the salts of the metal are preferably the same, although this is not critical and in some instances advantages may accrue as a result of using different metal salts. The preferred anions are the chlorides, bromides and nitrates, and the use of the chlorides is especially preferred. In some instances complexes of the metal, e.g., sodium chloropallidite and chloroplatinic acid can be used. Aqueous solutions are preferred, although other solvents can be employed. Usually, the concentration of the metal salts in the solution will range from 1 to 50%, preferably from 2 to 25%, by weight based on the total weight of the solution. The pH of the solution may for example vary from 1 to 7. When two or more metals are to be deposited they may be present in different amounts and deposited simultaneously or sequentially. This step is generally carried out under ambient conditions of temperature and pressure, though these operating conditions are not critical.

After the carrier pellets have been contacted with the metal compound solution, they are usually subject to reduction treatment to convert the metal compounds to the catalytically active metals. Conventional reduction procedures and agents such as hydrogen, carbon monoxide, and diborane may be utilized. Thermal decomposition of the metal compounds as well as direct reduction in aqueous or non-aqueous suspension by such materials as aqueous alkaline formaldehyde, aqueous hydrazine, aqueous or alcoholic sodium borohydride, or metallic sodium can also be employed where appropriate. The use of molecular hydrogen at temperatures ranging from about 150° to 250°C . is especially preferred, because of the simplicity.

In some instances it has been found advantageous to wash the reduced catalyst particles with deionized water one or more times to remove excess base or by-products formed by reduction of the metal compounds. If this expedient is employed, the catalyst is finally dried, e.g. at temperatures of from 80° to 150°C . under an inert atmosphere or under reduced pressure.

An alternative procedure involves omitting the drying step following the treatment of the carrier pellets with the alkaline solution and prior to contacting with the metal com-

pound solution. This omission is made possible by carefully controlling the method of treating the carrier pellets with the alkaline solution so that the resulting pellets have a water or alcohol content of from 25 to 90%, preferably 25 to 75%, of saturation. This is most easily effected by spray coating the carrier pellets with the alkaline solution.

The amount of time required to deposit the metals on the inert carrier in accordance with the method of this invention can be less than 2 hours, which is considerably shorter than previous deposition methods. It will be understood that the use of the spray coating technique for the application of the alkaline solution and of the metal compound solution provides the most direct and quickest method for carrying out the method of this invention. The treatment of the carrier pellets with the alkaline solution may take 20 to 30 minutes; the intermediate drying step, if necessary, may take 10 to 20 minutes; and the final spray coating step may take another 20 to 30 minutes.

Catalysts which may be prepared in accordance with the method of this invention include, for example, supported metals such as palladium, platinum, ruthenium, rhodium, iridium, osmium, titanium, gold, cobalt, nickel, tungsten, or mixtures thereof. Other metals which may be deposited therewith include, for example, iron and copper. Examples of mixed catalysts are palladium-platinum, palladium-silver, platinum-gold, nickel-silver, silver-mercury, and molybdenum-tin.

The catalysts produced by the practice of the method of this invention can be used, according to the metals deposited, in various catalytic processes such as oxidation, polymerization, hydrogenation, dehydrogenation, hydrocracking, epoxidation, and vinylation.

Certain supported catalysts of this invention have been found to have special applicability to the recently proposed processes for the preparation of vinyl acetate from ethylene. Such catalysts include palladium, palladium-platinum, and palladium-gold.

The vinyl acetate process involves the reaction of ethylene, oxygen and acetic acid in the presence of a Group VIII noble metal catalyst. It has been customary to activate the catalyst prior to its use in the synthesis reaction by adding thereto a minor amount of at least one alkali metal or alkaline earth metal organic acid salt or inorganic acid salt. The amount of activator added may for example range from 0.1 to 15%, preferably from about 1 to 7%, by weight based on the total weight of the metal and carrier. The alkali metal or alkaline earth metal salts of weak acids, both organic and inorganic acids, have been found to be especially useful as activators. Sodium, lithium, potassium, rubidium and caesium salts and mixtures

thereof have been found to be most effective, and the use of sodium and potassium salts, e.g., sodium and potassium acetates is especially preferred. Ordinarily, the useful activator salts will be those whose aqueous solutions have a pH greater than 7 or whose ionization constant is less than 10^{-1} . The salts may have such anions as citrate, acetate, borate, phosphate, tartrate, benzoate, or aluminate. The use of alkali metal or alkaline earth metal hydroxides has also proven to be effective. The use of halide anions should be avoided, since the presence of halides deleteriously affects the synthesis reaction.

The vinylation process is generally carried out at a temperature between 0° and $350^{\circ}\text{C}.$, and preferably from 50° to $250^{\circ}\text{C}.$; and under pressure conditions that may range from 15 to 1500 psi. absolute, and preferably at a pressure within the range of 15 to 250 psi. absolute. It will be understood, however, that neither the temperature nor the pressure conditions are considered to be critical.

The vinyl acetate process is conducted either in liquid trickle or vapor phase, and the latter mode of operation is preferred. When operating in the vapor or gaseous phase, the feed material comprising ethylene, oxygen and acetic acid vapors are passed into the reaction zone containing the catalyst. The vaporous reaction product mixture recovered from the reaction zone is treated to remove the vinyl acetate therefrom and the unreacted feed material recycled. The vinylation synthesis can be conducted in either a continuous or semi-continuous manner.

Although the vinylation process has been described above with respect to the use of ethylene for the preparation of vinyl acetate it will be understood that it is applicable to the production of other unsaturated esters from other olefinically unsaturated compounds and/or other carboxylic acids. Thus alkenes having from 2 to 18 carbon atoms per molecule may be employed to prepare the corresponding unsaturated organic esters. Illustrative alkenes include ethylene, propylene, butene-1, butene-2, isobutylene, octadecene-1, pentene-2, pentene-3, and the like. Other unsaturated hydrocarbons which may be employed in the process of this invention include butadiene, styrene, p-chlorostyrene, allyl acetate, allyl benzene, ethyl acrylate, hexadiene-1,5, as well as mixtures of one or more of the above compounds.

Acetic acid is the preferred organic acid utilized in the synthesis. However, other acids which may be employed include chloroacetic, phenyl acetic, propionic, isobutyric, benzoic, p-toluic, lauric, palmitic, stearic, and mixtures thereof. Thus the free

organic acid may have the formula $R'COOH$ wherein R' is a substituted or unsubstituted, branched or straight chain, aliphatic, cycloaliphatic or aromatic radical preferably having between 1 and 10 carbon atoms per molecule.

The invention will be more fully understood by reference to the following illustrative embodiments, which also show the use of the aforementioned catalysts in the production of vinyl acetate.

Example 1

A. Two hundred grams of $\frac{1}{8} \times \frac{1}{8}$ " alpha alumina pellets were covered with about 200 ml. of a solution 5 wt. % aqueous NaOH then drained free of excess solution. This procedure was repeated 5 times over a period of thirty minutes. The pellets were dried under a stream of warm air while rotating in an open dish until they just tumbled freely. The weight of absorbed hydroxide solution in the saturated pellets was determined and then approximately $\frac{1}{2}$ of the water present was evaporated under a stream of warm air. The pellets were then spray coated while tumbling with a solution of 3.39g. $PdCl_2$, 2.04g. $HAuCl_4$, $3H_2O$ and 2.0g. NaCl in 35 ml. water representing just enough water to return the pellets to their saturation point. The coated pellets were dried under a stream of nitrogen at $120^\circ C$., hydrogen reduced at $200^\circ C$., then exhaustively washed with deionized water. The reduction and washing procedure were

then repeated and finally the catalyst was dried at $100^\circ C$. and 0.1 mm. Hg.

Four additional batches of catalyst were prepared by the procedure used above and using the same reagents as above except that in each case a different pre-coating wash was employed. The pre-spray washes were (B) 2.5 wt. % Na_2CO_3 plus 2.5 wt. % NaOH, (C) 5 wt. % Na_2CO_3 , (D) 2.5 wt. % NaOH, (E) 1 wt. % NaOH.

Cross sections of representative samples of each of the above batches of catalyst were examined under magnification and the per cent of penetration of the metals of each batch was determined using a calibrated scale on the eyepiece of the microscope. The values shown in the table below are the average per cent penetrations observed of the metals to the center of the pellet based on examination of 10 samples of each batch.

B. The activity of each batch of catalyst in the vapor phase synthesis of vinyl acetate was determined on 5g. samples of each treated with 0.1g. of potassium acetate from aqueous solution. The activities were determined by passing 2 liters per hour of 15% oxygen in ethylene, saturated in acetic acid at $75^\circ C$., over the catalyst at atmospheric pressure and held at $140^\circ C$. The activities of each were determined after 72 hours continuous operation by condensing exit samples in a dry ice-isopropanol bath and analysis by gas liquid chromatography. The activity values shown in Table I are in grams of vinyl acetate produced per hour per gram of palladium.

TABLE I

Pre-coating Wash	Penetration	Activity
A 5% NaOH	4%	12.1
B 2.5% NaOH + 2.5% Na_2CO_3	17%	13.6
C 5% Na_2CO_3	37%	14.0
D 2.5% NaOH	50%	12.1
E 1% NaOH	100%	7.6

Example 2

Four additional batches of 200g. each of the same alumina support used in Example 1 were washed with the alkaline solution noted in Table II, below. These washed tablets were then spray coated with 1.70g. $PdCl_2$, 0.124g. $HAuCl_4$, $3H_2O$ and 1.0g. of NaCl

dissolved in 35 ml. of deionized water; then hydrogen reduced and washed as described in Example 1. The per cent penetration of the metals and the activities of each batch of catalyst after 24 hours continuous operation were determined as in Example 1. Results are shown in Table II.

TABLE II

Pre-coating Wash	Penetration	Activity
F 5% NaOH	2%	14.8
G 5% Na_2CO_3	13%	16.7
H 5% $NaHCO_3$	25%	18.0
I $2\frac{1}{2}$ % $NaHCO_3$	50%	8.4

Example 3

Two hundred grams of $\frac{1}{8} \times \frac{1}{8}$ " alpha alumina pellets were sprayed while tumbling

with 10% aqueous sodium hydroxide until they had gained approximately 40g. in weight. These base treated pellets were

immediately sprayed with the metal compound solution employed in Example I and were reduced by the same procedure as in Example 1. The penetration of the pellets by the metals, determined as described in Example 1 was 3 per cent.

Example 4

Two hundred grams of $\frac{1}{8} \times \frac{1}{8}$ " alpha alumina pellets were washed with 5% NaOH in methanol then were dried under a stream of warm air until 40% of the weight of the absorbed solution had been evaporated. These base treated pellets were then sprayed with the solution employed in Example 1 and were reduced by the same procedure as in Example 1. The penetration of the pellets by the metals, determined as described in Example 1, was 5 per cent.

Example 5

Two hundred grams of $\frac{1}{8} \times \frac{1}{8}$ " alpha alumina pellets were treated with 5% aqueous NaOH then partially dried as described in Example 1. The pellets were then sprayed until saturated with 3.15g. of AgNO₃ and 1.62 of Hg(NO₃)₂ in 45 ml. of water. The pellets were again partially dried until about $\frac{1}{2}$ of the water had been removed and the remaining solution was applied by spraying. Fifteen grams of the coated pellets were placed into 50 ml. of water containing 2.5g. of NaOH and 1 ml. of 99% hydrazine hydrate at 60°C. After 1 hour at 60°C. the reduced pellets were thoroughly washed with water then both then reduced and non-reduced pellets were dried at 90-100°C. and 0.1 mm. The penetration of the pellets by the metal of both the reduced and the non-reduced pellets was 2 per cent.

Example 6

Two hundred grams of $\frac{3}{8} \times \frac{1}{8}$ " alpha alumina tablets were treated with 5% aqueous NaOH then partially dried as described in Example 1. The pellets were then sprayed with 8.18g. of NiCl₂ · 6H₂O and 2.04g. HAuCl₄ · 3H₂O in 35 ml. of water. On completion of the coating (a) one-half of the pellets were reduced with hydrogen as in Example 1. In addition, 15g. portions were reduced with (b) 50 ml. of water containing 2.5g. of NaOH and 1 ml. of 99% hydrazine hydrate at 25 to 80°C. for 1 hour and (c) 50 ml. of water containing 2.5g. of NaOH and 1 ml. of 37% formaldehyde at 25 to 80°C. for 1 hour. All three catalysts showed a penetration of the pellets by the metal of 2 per cent.

Example 7

Two hundred grams of $\frac{1}{8} \times \frac{1}{8}$ " alpha alumina pellets were washed with 5 wt. % aqueous Na₂CO₃ and dried until they

tumbled freely as described in Example 1. The weight of the adsorbed Na₂CO₃ solution was determined and then 10 per cent of the water present was evaporated. The pellets were then alternately sprayed and dried using the metal compound solution employed in Example 1 maintaining the catalyst between 90 and 100 per cent saturated throughout this procedure. Eight spray and dry cycles were required to complete the coating. The coated pellets were hydrogen reduced and then the penetration of the pellets by the metals was determined as in Example 1. The average penetration was 5 per cent.

The above data show that the method of this invention can be utilized effectively to prepare metal catalysts supported on an inert carrier. In addition, the method affords the additional advantage of permitting control over the degree that the metals will penetrate the inert carrier particles. The importance of this feature is demonstrated in connection with the vinyl acetate synthesis process wherein the degree of penetration is an important factor in the activity of the catalyst. Thus with only peripheral penetration or with penetration that exceeds 50%, substantial decreases in catalytic activity is noted.

WHAT WE CLAIM IS:—

1. A method of preparing a supported metal catalyst which comprises depositing at least one metal compound on a porous catalyst support by contacting the support with a solution of at least one compound of at least one metal selected from platinum, ruthenium, rhodium, palladium, iridium, osmium, rhenium, vanadium, titanium, tungsten, molybdenum, gold, silver, cobalt, nickel and the lanthanide metals, and converting the deposited compound or compounds to the metallic state, the porous catalyst support contacted with the said solution being one which has been impregnated with an alkaline solution and which is from 25 to 90% saturated with water or an alcohol.

2. A method according to claim 1 wherein the porous catalyst support contacted with the metal compound solution is from 25 to 75% saturated with water or an alcohol.

3. A method according to claim 1 or 2 wherein the said metal compound solution additionally includes at least one compound of at least one metal selected from chromium, manganese, iron, copper, cadmium, tin, lead, aluminium and mercury.

4. A method according to any of claims 1 to 3 wherein the metal compound solution is spray-coated onto the carrier.

5. A method according to any of claims 1 to 4 wherein the support is one which has been impregnated with the alkaline solution by spraying therewith.

65

70

75

80

85

90

95

100

105

110

115

120

125

6. A method according to any of claims 1 to 5 wherein the support is one which has been impregnated with an aqueous alcoholic alkaline solution.
- 5 7. A method according to claim 6 wherein the support is one which has been saturated with the alkaline solution and dried to from 25 to 90 weight % saturated with water or alcohol.
- 10 8. A method according to claim 6 wherein the support is one which has been impregnated with an amount of the alkaline solution sufficient only to render the support from 25 to 90 weight % saturated with water or alcohol.
- 15 9. A method according to any of claims 1 to 8 wherein the support comprises alumina.
- 20 10. A method according to any of claims 1 to 8 wherein the support comprises silica or carbon.
- 25 11. A method according to any of claims 1 to 10 wherein the alkaline solution is a solution of one or more of ammonium phosphate and alkali metal acetates, hydroxides, carbonates, bicarbonates and hydrogen phosphates.
- 30 12. A method according to claim 11 wherein the alkaline solution is a solution of sodium hydroxide.
- 35 13. A method according to claim 11 wherein the alkaline solution is a solution of sodium carbonate.
- 40 14. A method according to any of claims 1 to 13 wherein the metal compound solution is an aqueous solution.
15. A method according to any of claims 1 to 14 wherein palladium and gold compounds are deposited on the support and converted to the metals.
16. A method according to any of claims 1 to 14 wherein palladium and platinum compounds are deposited on the support and converted to the metals.
17. A method according to claim 1 for preparing a supported metal catalyst, substantially as hereinbefore described in any one of Examples 1 to 7.
18. A supported metal catalyst prepared by a method according to any one of claims 1 to 17.
19. A catalyst according to claim 18 containing a Group VIII noble metal.
20. A catalyst according to claim 19 containing an alkali metal or alkaline earth metal hydroxide or salt of a weak acid.
21. A catalyst according to any of claims 18 to 20 in the form of pellets, the degree of penetration of metal into the pellets being up to 50% of the pellet radius.
22. A process for the preparation of an unsaturated ester which comprises reacting an olefinically unsaturated compound with a carboxylic acid and molecular oxygen in the presence of a catalyst according to any of claims 18 to 21 which contains a Group VIII noble metal.
23. A process according to claim 22 wherein ethylene, molecular oxygen and acetic acid are reacted to prepare vinyl acetate.
24. A process according to claim 23 wherein the catalyst contains palladium metal.
25. A process according to claim 24 wherein the catalyst contains gold metal.
26. A process according to any of claims 23 to 25 conducted in the vapor phase.
27. A process according to claim 22 for preparing vinyl acetate, substantially as described in Example 1 or 2.
28. Vinyl acetate prepared by a process according to any of claims 23 to 27.
- REDDIE & GROSE,
Agents for the Applicants,
6, Bream's Buildings,
London, E.C.4A 1HN.